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(54) **Austenitic alloy steel and bar, billet, wire, slab, plate, sheet, tube or forgings.**

(57) An austenitic alloy of iron, chromium, nickel and aluminium containing
15 to 20% chromium,
15 to 20% nickel and
0 to 5% cobalt but the content of nickel
and cobalt being such that $(\frac{Co}{2} + Ni)$ is from 15 to 20%,
where Co is the percentage of cobalt, and Ni is the percentage of nickel,
2 to 4 % aluminium,
0.02 to 0.15% carbon,
0.1 to 0.8 % titanium,
0.2 to 2.0 % silicon,
0.2 to 2.0 % manganese,
and optionally from 0 to 0.8% of hafnium or of zirconium the balance being iron and incidental amounts of other alloying elements.

The alloy provides resistance to oxidation and sulphidation together with weldability and hot strength.

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# AUSTENITIC ALLOY STEEL AND BAR, BILLET, WIRE, SLAB, PLATE, SHEET, TUBE OR FORGINGS

The present invention relates to austenitic alloys or iron, chromium and nickel, containg additions of aluminium and titanium, with or without additions of either hafnium or zirconium.

The present invention provides an austenitic alloy of iron, chromium, nickel and aluminium containing

15 to 20 % chromium,
15 to 20 % nickel and
0 to 5 % cobalt but the content of nickel and cobalt being such that $(\frac{Co}{2} + Ni)$ is from 15 to 20% where Co is the percentage of cobalt, and Ni is the percentage of nickel,
2 to 4 % aluminium,
0.02 to 0.15 % carbon,
0.1 to 0.8 % titanium,
0.2 to 2.0 % silicon,
0.2 to 2.0 % manganese,

and optionally from 0 to 0.8 % of hafnium or of zirconium the balance being iron and incidental amounts of other alloying elements.

In our British Patent applications Nos.8006738 and 8006739 we disclosed ferritic alloys of iron, chromium and aluminium containing titanium and hafnium

respectively and providing resistance to oxidation. It has been found that the ferritic alloys described in these applications, although possessing adequate oxidation and/or sulphidation resistance, have insufficient hot strength for use in some environments or fail to find application due to their inherently poor welding and fabricating characteristics.

Those skilled in the art will appreciate that a sufficient amount of chromium must be present to provide a basic oxidation resistance. On the other hand, since a low nickel content is desirable from the point of view of sulphidation resistance, to maintain an austenitic structure the chromium content should be kept to the minimum consistent with adequate oxidation resistance. The additional benefit contributed by small but significant additions of either hafnium or zirconium does in some instances appear worthwhile. The provision of titanium stabilises the alloy against intercrystalline corrosion effects. A high silicon content, whilst possibly being beneficial as regards oxidation resistance, is to be avoided on account of its possible embrittlement effect. Similarly, a sufficiently high manganese content to be effective as a delta ferrite suppressor is not advisable on account of its detraction from

oxidation resistance.

Up to 5% of cobalt is permitted, fulfilling essentially the same purpose as nickel. When cobalt is present it can be regarded as a replacement on a 2:1 basis for nickel.

Optionally up to 0.8%, e.g. 0.05 to 0.80%, of hafnium or of zirconium may be included. The balance of the composition is iron and incidental amounts of other alloying elements not specifically added. The presence of incidental amounts of copper, cobalt, molybdenum and tungsten above the impurity level may be tolerated provided they are not present in excess. Other elements such as sulphur and phosphorus may be present but these are impurities which are not desirable.

In all cases, however, the composition balance is such as to ensure a virtually non-magnetic alloy.

The alloys may be manufactured by processes normally used for making alloys of this general type. For instance, they may be made by induction melting, either in air or using inert atmosphere or vacuum as appropriate, cast into ingots and subsequently forged or rolled into billet or slab prior to working down to plate, sheet, strip, bar wire, tube or any other commercially saleable form.

In a typical small scale process for producing an austenitic steel of this invention, a charge of high purity iron, nickel pellet and low carbon ferrochromium is melted down in a basic lined induction furnace, either in air under a base slag, or under an inert atmosphere or in vacuo, without slag, as appropriate. When completely melted, the appropriate additions of aluminium, ferrotitanium (and hafnium or zirconium or other special metal addition) are added, in that order, the metal brought to temperature and cast into an appropriate ingot mould.

The invention will be illustrated by the following examples. Alloys according to the invention were prepared having the compositions given below by the process described above. The size of the melts was 10 kg each, giving a 2½" (60 mm) square ingot which was heated to 1150° C and forged under a 10 cwt. hammer to produce suitable test bar.

| Example | C | Si | Mn | Cr | Ni | Al | Ti | Hf |
|---|---|---|---|---|---|---|---|---|
| A | 0.077 | 0.73 | 0.95 | 17.64 | 17.40 | 2.48 | .41 | - |
| B | 0.078 | 0.72 | 0.95 | 17.68 | 17.48 | 2.48 | .39 | - |
| C | 0.064 | 0.74 | 0.94 | 17.52 | 17.48 | 2.70 | .41 | .52 |

The resistance of these steels to oxidation was compared by the following test procedure:

Specimens some ½" (13 mm) in diameter by 1¼" (30 mm) long were machined from bar and ground to a 120 grit finish. They were washed and cleaned in alcohol prior to test.

The test was of relatively short duration but involved cycling between ambient and test temperature. The test chamber was an alumina tube 2" (50 mm) internal diameter in which the sample was positioned across an open ended alumina boat. Heating was by means of the concentric electric furnace, the temperature being measured by reference to a noble metal thermocouple, the hot junction of which was immediately above the specimen. The test atmosphere was produced by burning natural gas using excess air over that required for combustion, the flow rates being 1.4 cubic foot and 14 cubic foot (0.04 and 0.4 cubic metres) per hour respectively for gas and air. The combustion product, a mixture of nitrogen, oxygen, carbon dioxide and steam, was preheated to test temperature before passing through the test chamber;

test temperature was established prior to inserting the sample so that heating was rapid. Each test cycle was for six hours; after this the specimens were removed from the test chamber and cooled in a closed container so that any scale which became detached was collected. When cold, the specimen was weighed, together with any detached scale and then scrubbed with a stiff bristle brush to remove any loosely adherent oxide prior to reweighing to obtain the starting weight for the next cycle. The whole procedure was repeated for a total of seven cycles and the total gain in weight, that is the sum of the individual gains, expressed as milligrams per square centimetre for the 42-hour period, using the original surface area for the untested specimen, was taken as the scaling index.

The scaling indices for the steels tested were as follows:

| | Example A | Example B | Example C | Typical AISI 310 |
|---|---|---|---|---|
| 1100°C | 7.7 | 2.3 | 4.3 | 6 |
| 1150°C | 52.3 | 30.5 | 34.2 | 11 |
| 1200°C | 119.3 | 66.6 | 103.1 | 17 |
| 1250°C | 133.0 | 141.1 | 146.9 | 30 |

Thus for service at temperatures up to 1100°C in oxidising atmospheres the alloys covered by the present application are at least equivalent to the standard material known as AISI 310. None of the materials were suitable for use at higher temperatures.

To make a rough assessment of resistance to sulphidation, similar test specimens to those used above were prepared and weighed and then half immersed in an intimately ground mixture of 90% sodium sulphate and 10% sodium chloride contained in alumina boats. These were then placed on a stainless steel tray, with samples of a number of other different materials similarly treated, and the whole placed in a muffle furnace and heated to 900°C for six hours. The tray was then withdrawn, the samples allowed to cool, cleaned as far as possible in hot water and then cathodically descaled in a bath of molten sodium hydroxide at 350°C, using a current of 9 amperes for 20 minutes. After descaling and thorough washing, they were dried in alcohol and reweighed. Losses in weight, expressed in mgm. per sq.cm., were as follows:-

| Example | Weight Loss |
| --- | --- |
| A | 4.4 |
| B | 1.3 |
| C | 2.2 |

These figures were as low as those found with any other steel tested, including the special iron-chromium-aluminium alloys of our copending applications referred to above. In general, alloys with high nickel contents but not containing aluminium failed catastrophically, examples being:

| Sample | Weight Loss |
| --- | --- |
| A.I.S.I.310 (25 Cr-20 Ni) | 1114 |
| Ni-Cr Alloy (80 Ni-20 Cr) | 1447 |

To check the relative hot strengths of the proposed materials, hot tensile tests were carried out at a number of temperatures, with a strain rate of three inches per minute. These indicated the hot strength to be similar to that of A.I.S.I.310 and considerably higher than that of the iron-chromium-aluminium alloys.

Laboratory scale welding trials, with deposits laid down on the edges of 1" x¼" coupons, indicated freedom from cracking within the parent metal.

The alloys exemplified above can be seen to

provide a weldable, relatively strong series of alloys, similar in general characteristics to the well known A.I.S.I.310 heat resisting material but having the advantage of resistance to sulphidation attack exhibited by the iron-chromium-aluminium alloys. Alternatively, they exhibit the resistance to sulphidation attack of the iron-chromium-aluminium alloys but have the advantage over these of higher hot strength and weldability, making them suitable for tube manufacture for use in difficult environments without the need for cladding and rendering them capable of being used in welded fabrications, their only disadvantage being a lower resistance to pure oxidation as compared with the more advanced iron-chromium-aluminium alloys. These latter properties, however, can only adequately be realised with adequate support in applications such as electric resistance elements.

CLAIMS:

1. An austenitic alloy of iron, chromium, nickel and aluminium characterised by containing

15 to 20 % chromium,

15 to 20 % nickel and

0 to 5 % cobalt but the content of nickel and cobalt being such that $(\frac{Co}{2} + Ni)$ is from 15 to 20% where Co is the percentage of cobalt, and Ni is the percentage of nickel,

2 to 4 % aluminium,

0.02 to 0.15 % carbon,

0.1 to 0.8 % titanium,

0.2 to 2.0 % silicon,

0.2 to 2.0 % manganese,

and optionally from 0 to 0.8 % of hafnium or of zirconium the balance being iron and incidental amounts of other alloying elements.

2. An alloy as claimed in claim 1 further characterised by containing from 17 - 20% chromium.

3. An alloy as claimed in claim 1 or Claim 2 further characterised by containg 17 - 20% nickel.

4. An alloy as claimed in any preceding claim further characterised by containing titanium such that the content is not less than 4 times the carbon content but not more than 0.8%.

5. An alloy as claimed in any preceding claim further characterised by containing about 2.5% aluminium.

6. An alloy as claimed in any one of claims 1 to 5 further characterised by containing 0.05 to 0.8% hafnium.

7. An alloy as claimed in any one of claims 1 to 5 further characterised by containing 0.05 to 0.8% zirconium.

8. Bar, billet, wire, slab, plate, sheet tube or forgings characterised by being in an alloy as claimed in any one of the preceding claims.

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# EUROPEAN SEARCH REPORT

| Category | DOCUMENTS CONSIDERED TO BE RELEVANT<br>Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3) |
|---|---|---|---|
| | GB - A - 1 361 055 (SUMITOMO KINZOKU KOGYO K.K.)<br>* claim 1 *<br>-- | 1,4,7 | C 22 C 38/50 |
| | GB - A - 371 334 (S.A. DE COMMENTRY FOURCHAMBAULT & DECAZEVILLE)<br>* claims 1,2 *<br>-- | 1 | |
| | GB - A - 404 876 (S.A. DE COMMENTRY FOURCHAMBAULT & DECAZEVILLE)<br>* claim 1 *<br>-- | 1 | TECHNICAL FIELDS SEARCHED (Int.Cl. 3)<br>C 22 C 38/50<br>38/52<br>38/40 |
| | DE - A - 2 648 968 (NIPPON STEEL CORP.)<br>* claims 1,7 *<br>-- | 1 | |
| | SU - A - 589 281 (KAZIMIROVSKAIA et al.)<br>* claim *<br>-- | 1 | CATEGORY OF CITED DOCUMENTS<br>X: particularly relevant if taken alone<br>Y: particularly relevant if combined with another document of the same category<br>A: technological background<br>O: non-written disclosure<br>P: intermediate document<br>T: theory or principle underlying the invention<br>E: earlier patent document, but published on, or after the filing date<br>D: document cited in the application<br>L: document cited for other reasons |
| A | GB - A - 465 916 (HATFIELD et al.)<br>* claim 1 *<br>-- ./. | 1 | &: member of the same patent family, corresponding document |

X The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 25-01-1982 | LIPPENS |

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# EUROPEAN SEARCH REPORT

Application number
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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl.[3]) |
|---|---|---|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| A | GB - A - 1 570 026 (HENRY WIGGIN & CY. LTD.)<br>* claim 1; page 2, lines 28-31 *<br>---- | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.[3]) |